Defect control in zinc oxynitride semiconductor

for high-performance and high-stability thin-film transistors

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Abstract. The fabrication of thin-film transistor devices incorporating active semiconductors based on zinc oxynitride (ZnON) compound is presented. It is demonstrated that the addition of appropriate dopant, gallium, in ZnON, suppresses the formation of shallow donor, nitrogen vacancies, and significantly improves electrical characteristics of the resulting TFT. The Ga:ZnON devices with field-effect mobility values exceeding 50 cm^2/Vs are achieved, which makes them suitable as switching or driving elements in next-generation flat-panel displays.

Introduction

Increasing demands for high performance switching or driving transistors in the flat panel display industry have led to the development of high mobility metal oxide semiconductors such as In-Ga-Zn-O (IGZO) and Hf-In-Zn-O (HIZO) [1,2]. Thin-film transistors (TFT) that incorporate such materials exhibit field effect mobility, exceeding 10 cm^2/Vs, and are suitable for the fabrication of ultra high definition (4000 x 2000 pixels), large size (> 70 inch) displays operating at extremely high frame rates (> 480 Hz). However, further advances in display technology aim at producing 3D images or driving organic light-emitting diodes (OLED) while satisfying the above criteria. In this regard, transistors with even higher field effect mobility (> 30 cm^2/Vs) must be integrated in the backplane array [3].

In the present article, a recent work on a relatively new type of semiconductor, namely zinc oxynitride (ZnON) [4,5] as a promising candidate for the next-generation display applications, will be presented. The deposition of ZnON films involves reactive magnetron sputtering using a zinc metal target, using plasmas that contain a proprietary mixture of argon, oxygen and nitrogen. TFT devices with field effect mobility close to 100 cm^2/Vs (comparable to those of poly-silicon TFT) are routinely achieved by the proper adjustment of deposition parameters. However, TFTs based on ZnON inherently suffer from the large number of nitrogen vacancies which needs to be reduced [5].

Here, it is theoretically suggested that dopants such as gallum (Ga) act as carrier suppressors in ZnON matrix based on first-principles calculation, by suppressing the formation of nitrogen vacancies. Indeed, the effects of Ga-doping in ZnON were experimentally demonstrated in electrical measurements of thin films as well as TFT devices.

Methods

The density-functional theory (DFT) calculations were performed as implemented in the Vienna *ab initio* simulation package (VASP) code [6,7]. The projector-augmented wave (PAW) pseudopotentials [8] and the plane-wave basis set with a kinetic energy cutoff of 500 eV were used.

The generalized-gradient-approximation (GGA) [9] with the on-site Coulomb energy (U) of 8 and 7.5 eV for Ga and Zn d states [10] (GGA + U), respectively, was mainly used for the exchange correlation energy. The 320-atom supercell for Zn_3N_2 (cubic anti-bixbyte structure) with $2\times2\times2$ in the x,y,z directions obtained by repeating the optimized structure of perfect unit cell was used in the defect calculations. We used a $2\times2\times2$ special-k-point mesh for integrations over the Brillouin zones.

To fabricate TFT devices, 200 nm-thick molybdenum (Mo) was sputtered on Eagle glass substrates and patterned photolithographically to form the gate electrodes. Then, a stack of a 350 nm-thick silicon nitride (SiN_x) and 50 nm-thick silicon oxide (SiO_x) was deposited sequentially by plasma-enhanced chemical vapor deposition (PECVD) to form the gate insulator. After etching the via holes by photolithography, 50 nm-thick ZnON active layers were deposited by reactive radio frequency (rf) sputtering. A zinc metal target was used, and the film growth occurred in a mixture of argon (Ar, 10 sccm), nitrogen (N_2, 100 sccm), and oxygen (O_2, 1 sccm) plasma. In order to dope the ZnON films, a separate gallium oxide (Ga_2O_3) ceramic target was used and cosputtered along with the zinc metal target. The power applied to the Ga_2O_3 target was intentionally modified so that the gallium content in the resulting film could be adjusted. Then, a 70 nm-thick aluminum (Al) film was deposited by thermal evaporation and patterned through a shadow mask to form the source and drain electrodes. The final device structure is illustrated schematically in Figure 4(a).

The electrical characteristics of the fabricated TFT devices were evaluated using a Keithley 4200-SCS parameter analyzer in air. Hall measurements were performed in order to study the electrical characteristics of the semiconductor films.

Results and Discussions

Figure 1 shows the fully optimized cell with the band gap of 0.56 eV to simulate the pure cubic Zn_3N_2 crystal. Several types of defects including vacancies, interstitials, and anti-sites in Zn_3N_2 were next studied.
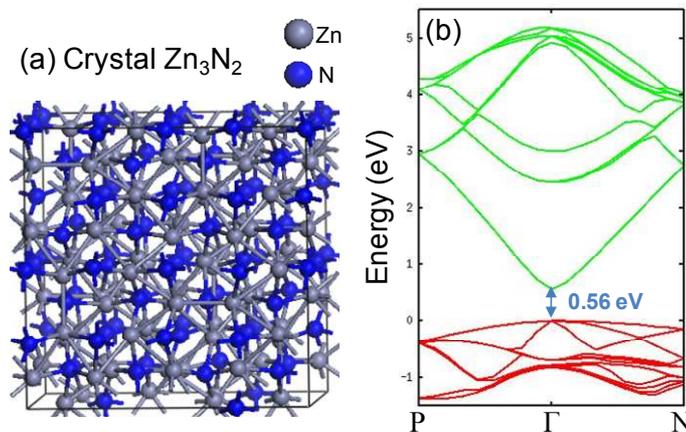
Figure 1. (a) Atomic model of c-Zn_3N_2. (b) The calculated band structure of c-Zn_3N_2.

The calculated formation energies of possible point defects in c-Zn_3N_2 are listed in Table 1. The smallest positive formation energy of 1.97 eV for nitrogen vacancy suggests that the formation of nitrogen vacancy is most favorable during synthesis of zinc nitride based system.

Figure 2 shows the total density of states (DOS) of perfect Zn_3N_2 and the total DOS of Zn_3N_2 with a nitrogen vacancy. For N vacancy system, the result clearly reveals that the N vacancy causes an impurity band near the edge of conduction band and the Fermi level (E_F) relocates near the bottom of conduction band, which is of n-type conduction character. Therefore, the major defects that act as sources of free carriers in zinc nitride system can be ascribed to nitrogen vacancies.

Table 1. Formation energies (in eV) of possible point defects in zinc nitride system.

Point Defect	V_N	V_{Zn}	Zn_i	N_i	Zn_N	N_{Zn}
Formation E (eV)	+1.97	+2.69	+5.19	+3.39	+5.39	+3.78

In order to control or suppress the formation of nitrogen vacancies in zinc nitride system, cation doping such as gallium and aluminum with relatively stronger cation-nitrogen bonds was studied. Our first principles calculations indeed indicate that the formation energy of nitrogen vacancies in Zn_3N_2 increases from 1.97 eV for pure system to 2.77 and 2.96 eV for Ga and Al doping, respectively. Also, the incorporation of gallium cations in zinc oxide is well known to have the same effect [1], thus gallium in ZnON acts as a carrier suppressor.
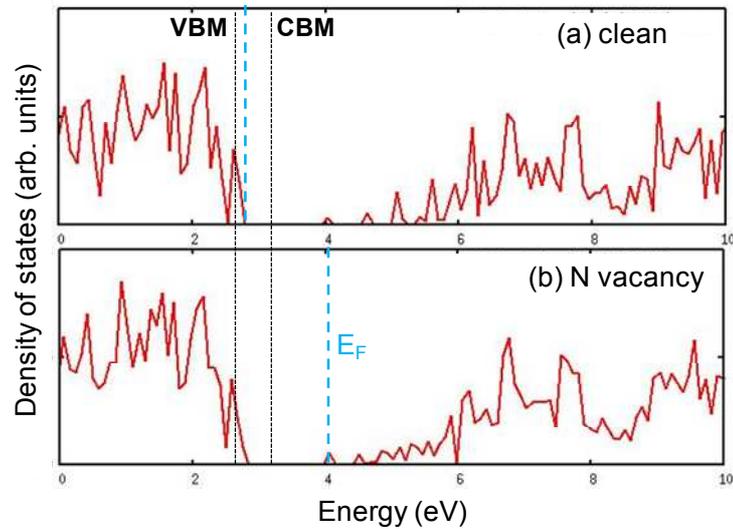
Figure 2. Calculated electronic density of states (DOS) of (a) the perfect Zn_3N_2 crystal and (b) the crystal containing nitrogen vacancy.

The effect of gallium as a carrier suppressor in ZnON was experimentally demonstrated next. Hall mobility and carrier concentration measurements were done on the ZnON films with respect to different Ga/Zn cation compositions, and are shown in Figure 3. As the Ga/Zn ratio increases in ZnON, the electron concentration significantly decreases by two orders magnitude and Hall mobility also decreases. The ZnON device characteristics are shown in Figure 4. As the gallium content increases, the off-current decreases, the threshold voltage shifts toward positive values, and the field-effect mobility decreases. Finally, ZnON TFT with Ga/Zn=4% exhibits the field-effect mobility of 62 cm^2/Vs and threshold voltage of -5 V.

More research is currently underway towards the integration of ZnON based semiconductors into TFT devices that are fabricated using a fully lithographic process. The basic device structure shall involve a bottom gate inverted staggered configuration, preferably incorporating an etch stopper layer. It is important to carefully optimize the etch selectivity of the materials adjacent to the ZnON semiconductor in order to properly pattern the etch stopper and source-drain electrodes.

Once the desired device performance in terms of field effect mobility (>50 cm^2/Vs), threshold voltage and subthreshold swing are obtained, the stability under negative or positive bias stress will be evaluated.
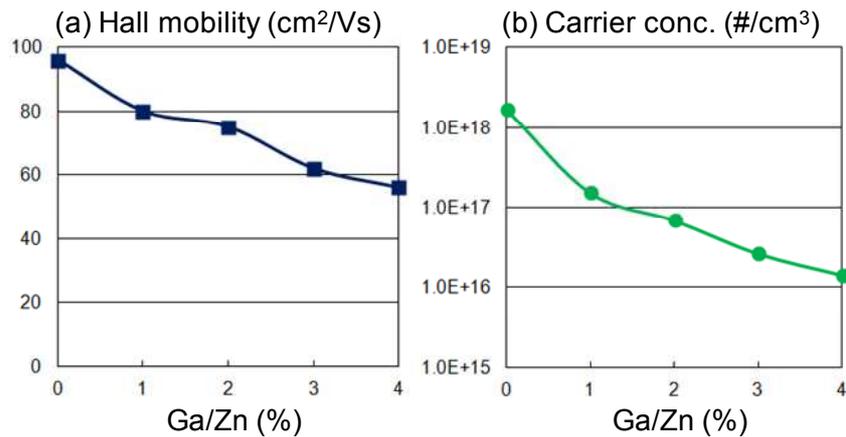
Figure 3. Hall measurement results on ZnON films with respect to the Ga/Zn cation ratio (a) Hall mobility. (b) Carrier concentration.
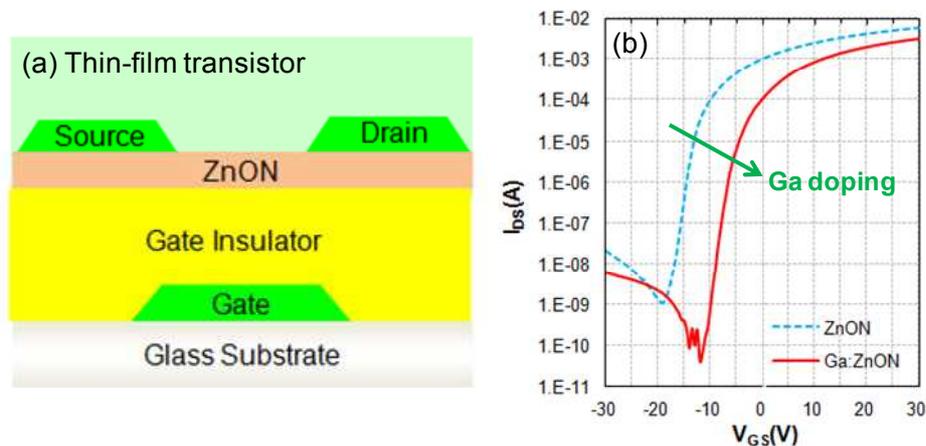
Figure 4. (a) Bottom gate thin-film transistor (TFT) device structure. (b) Transfer characteristics of ZnON TFT devices (Ga/Zn=0% and 4%).

Summary

Gallium doping in ZnON has a carrier suppressing effect, and it is suggested that this originates from the ability of gallium to form stronger Ga-N bonds than Zn-N bonds, which decreases the probability of having nitrogen vacancies that are the major source of free electrons.

Using the above semiconductors, TFT devices of field-effect mobility values exceeding 50 cm^2/Vs can be routinely fabricated and further process development is in progress to integrate ZnON materials using fully lithographic methods.

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